



# Development and costs calculation of lithium–sulfur cells with high sulfur load and binder free electrodes

M. Hagen<sup>a,\*</sup>, S. Dörfler<sup>b</sup>, P. Fanz<sup>a</sup>, T. Berger<sup>a</sup>, R. Speck<sup>a</sup>, J. Tübke<sup>a</sup>, H. Althues<sup>b</sup>,  
M.J. Hoffmann<sup>c</sup>, C. Scherr<sup>c</sup>, S. Kaskel<sup>b</sup>

<sup>a</sup> Fraunhofer Institute for Chemical Technology (ICT), Joseph-von-Fraunhofer-Str. 7, 76327 Pfinztal, Germany

<sup>b</sup> Fraunhofer Institute for Material and Beam Technology (IWS), Winterbergstraße 28, 01277 Dresden, Germany

<sup>c</sup> Karlsruhe Institute of Technology (KIT), Institute for Applied Materials, Ceramics in Mechanical Engineering, Haid- und- Neu-Straße 7, D-76131 Karlsruhe, Germany

## H I G H L I G H T S

- Binder free sulfur cathodes based on CNT for Li–S batteries.
- High sulfur loads.
- Influence of electrode surface and structure on electrochemical performance.
- Costs calculation for 18650 cell.

## A R T I C L E I N F O

### Article history:

Received 12 July 2012

Received in revised form

22 September 2012

Accepted 3 October 2012

Available online 10 October 2012

### Keywords:

Lithium–sulfur

Binder free

CNT

High sulfur load

Costs calculation

## A B S T R A C T

A binder free thick film sulfur cathode based on a carbon structure with carbon nano tubes (CNT) is introduced. The sulfur mass can be varied between 3 and 20 mg cm<sup>−2</sup> electrode leading to sulfur loads that are several times as high as in slurry electrodes. The electrode structure and thickness is examined by SEM, the surface area measured by BET and the in-plane conductivity is determined by a modified 4-point measurement. The achieved capacities for these extremely high sulfur loads are around 900 mAh g<sup>−1</sup> sulfur at a current of 0.64 mA cm<sup>−2</sup> electrode.

Additionally the price of future Li–S cells (18650), both conventional sulfur slurry cathode and here introduced binder free CNT sulfur cathode were calculated and compared with a lithium-ion system (NCA-graphite).

© 2012 Elsevier B.V. All rights reserved.

## 1. Introduction

Lithium–sulfur cells are regarded as one of the most promising systems for next generation batteries due to their high theoretical capacity, the abundant and cheap sulfur resources and lithium-ion comparable cathode production techniques. One great benefit vs. Li–O<sub>2</sub> is the encapsulated system which greatly reduces the complexity of a future Li–S cell and prevents parasitic influence from outside.

Drawbacks of Li–S are the low operating voltage of around 2.15 V during discharge, the isolating property of both sulfur and Li<sub>2</sub>S, the volume change of approximately 79% based on full

transformation of sulfur to Li<sub>2</sub>S, safety problems due to the lithium metal anode and a polysulfide shuttle mechanism first described by Mikhaylik et al. [1].

During the last ten years the electrochemical properties of the Li–S system have been greatly improved. Having only 10–20 cycles with low and unstable capacities at the beginning, the barrier of 100 relatively stable cycles with high capacities around 800–1000 mAh g<sup>−1</sup> sulfur have been reached in a recent publication [2]. An example for high cycle stabilities at high currents (1.3 mA cm<sup>−2</sup> = 1C; sulfur load: <1 mg cm<sup>−2</sup> electrode) with good capacities can be found in Schuster et al. [3].

Nevertheless most sulfur cathodes in the previous investigations had sulfur loads below 2 mg cm<sup>−2</sup> electrode [4]. Additionally, the sulfur fraction in sulfur electrodes is greatly below the common 80% active material level in lithium-ion cathodes. Fig. 1 gives the fraction of the active material in cathodes for recent Li–S

\* Corresponding author. Tel.: +49 721 4640 716; fax: +49 721 4640 318.  
E-mail address: [markus.hagen@ict.fraunhofer.de](mailto:markus.hagen@ict.fraunhofer.de) (M. Hagen).

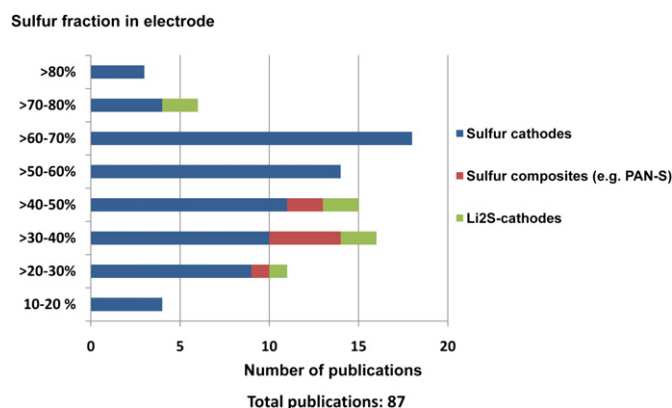


Fig. 1. Active material fraction in sulfur based cathodes out of 87 publications.

publications (total 87) during the last 10 years. Most of the evaluated work (84%) is about electrodes using elemental sulfur as active cathode material (indicated by ■ in Fig. 1); 8% used sulfur composite cathodes (indicated by ■ in Fig. 1) in which the sulfur was bonded to a conductive carbon chain (e.g. polyacrylonitrile + sulfur). The other 8% of the previous work are based on Li<sub>2</sub>S cathodes that can work without a lithium metal anode (indicated by ■ in Fig. 1). So it can be concluded that most of the cathodes and especially the sulfur composites have an active material fraction below 60%. Keeping in mind that the porosity of sulfur cathodes (that has to be filled with electrolyte) is regularly above 30% to sustain active material volume change ( $S_8 \leftrightarrow Li_2S$ : 78%), the gravimetric energy density of such a Li–S cell won't be above current lithium–ion level.

In order to obtain high energy densities it is important to have high sulfur utilization, high loads and high fractions of active material in the electrode. We therefore introduce a binder free thick film electrode based on CNT, coated on a conductive carbon structure that can contain very high loads of active material (3–20 mg cm<sup>−2</sup> electrode).

## 2. Experimental

### 2.1. Preparation of CNT-electrodes

A 3D carbon nonwoven-based gas diffusion layer (SGL Carbon, Sigracet GDL 10AA, weight: 8.5 mg cm<sup>−2</sup> ± 1.4 mg cm<sup>−2</sup>) with a dimension of approximately 6 × 20 cm was used as substrate for the growth of CNTs by a CVD process. The detailed procedure is described in Refs. [5,6]. Different series of CNT coated carbon structure electrodes were prepared by varying the CNT mass per cm<sup>2</sup> electrode in order to evaluate its influence on the electrochemical and physical electrode properties.

The electrodes were cut by a round punch hole with  $d = 10$  mm leading to an electrode surface of 0.785 cm<sup>2</sup>. The sulfur infiltration took place in air by adding sulfur powder homogeneously on the electrode and a subsequently melting of the sulfur on a hot plate at 150 °C to infiltrate the CNT structure. The whole process took about 1–2 min. The CNT mass and the sulfur mass of every single test electrode were weighed with a balance (Mettler Toledo XP205) having an accuracy of 0.01 mg and by calculating the difference between the bare carbon structure, the CNT coated carbon structure and the sulfur infiltrated CNT-carbon electrode.

### 2.2. Cell assembly and analysis

All tests were conducted against metallic lithium (Sigma Aldrich 99.9% purity) as counter electrode. The lithium was scraped with

a ceramic knife in order to remove surface layers and afterwards pressed through a calendar to obtain a homogeneous and reproducible surface. The cell assembly is comparable to typical Swagelok type cells with the difference that glass tube cells were used which allow the examination of the electrode stack and electrolyte. The corresponding cell design was developed by Fraunhofer ICT. As separator a Celgard 2400 (thickness: 25 μm, porosity: 41%) was used. A defined amount of electrolyte (0.7M LiTFSI in DME:DIOX (2:1, v:v) (Sigma Aldrich, anhydrous), 0.25M LiNO<sub>3</sub> (ABCR 99.98%; metals basis)) with a water content below 20 ppm was pipetted on the separator. The assembly of the test cells took place in an argon-filled glove box (MBraun) with an O<sub>2</sub> and H<sub>2</sub>O content below 1 ppm.

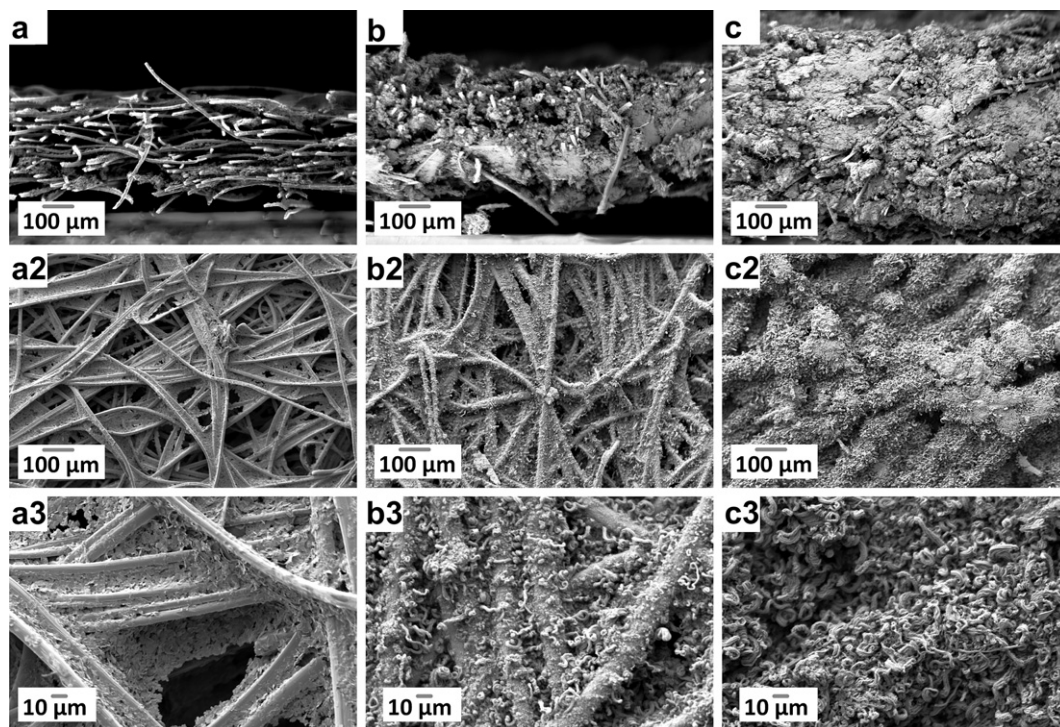
### 2.3. Characterization methods

- The CNT-S electrodes were cycled between 1.8 V and 2.8 V with an increasing current between 0.64 and 3.84 mA cm<sup>−2</sup>. The used cycle station was a Basytec CTS-LAB system.
- The CNT carbon structure electrode is characterized by a scanning electron microscope (SEM) (Zeiss type EVO MA 10) with a Peltier element cooled sample holder and wolfram cathode. The thickness of the electrodes was additionally measured with a constant pressure of 1.5 N leading to a force of 1.9 N cm<sup>−2</sup>.
- The in plane conductivity of the CNT coated carbon structures was measured by a self developed and modified 4-point device. Instead of contact tips two gold wires with defined distance were used. The carbon structure electrodes were cut with a length of 6 cm and width of 2 cm and were contacted by bonding two copper foils to each ends with silver conductive glue. Through the copper contacts a current of 100 mA was applied and the gold wires were pressed on the sample surface by hand. By measuring the voltage drop between the gold wires it was possible to calculate the specific conductivity of each sample. Variation of pressure by hand didn't change the conductivity results. Every measurement was repeated and led to the same results.
- Multi Point BET examinations were done with a Quantachrome Nova 2000e with nitrogen adsorption gas at 77 K and a pressure  $p/p_0 = 0-0.3$ . Before measuring the surface of the sulfur free CNT electrodes, the samples were heated to 200 °C in order to remove adsorbed water.

## 3. Results and discussion

### 3.1. CNT growth on carbon structure substrates

Fig. 2 shows scanning electron micrographs (SEM) of the received carbon structure (column a) and the CNT coated structures (column b with 4.7 mg cm<sup>−2</sup> electrode and column c with 11.0 mg cm<sup>−2</sup> electrode). The carbon fibres have a thickness of around 10 μm and build up a network with a distance of around 30–100 μm to the neighbouring fibres. It is clearly visible that the CNT coating increases the thickness of the electrode by pushing the carbon fibres apart. Additionally the high macro porosity of the carbon structure seems to be decreased by the CNT coating. A CNT mass of 4.7 mg cm<sup>−2</sup> electrode hides most of the fibres in the side view picture (Fig. 2b). A higher CNT mass of 11.0 mg cm<sup>−2</sup> electrode even conceals the complete electrode with exception of some carbon fibre tips that still look out of the CNT forest (Fig. 2c). Regarding the bird's eye view SEM pictures the carbon fibres can still be clearly identified for samples with a CNT mass of 4.7 mg cm<sup>−2</sup>, but a CNT mass of 11.0 mg cm<sup>−2</sup> leads to a complete coverage of the carbon fibre backbone. The CNT growth behaviour in dependence of the used catalyst is comprehensively discussed in Refs. [5,6].



**Fig. 2.** SEM – carbon structure in side view (a, b, c) and corresponding bird's eye view (a2, b2, c2, a3, b3, c3) with no CNT (a, a2, a3),  $4.7 \text{ mg cm}^{-2}$  CNT (b, b2, b3) and  $11.0 \text{ mg cm}^{-2}$  CNT (c, c2, c3).

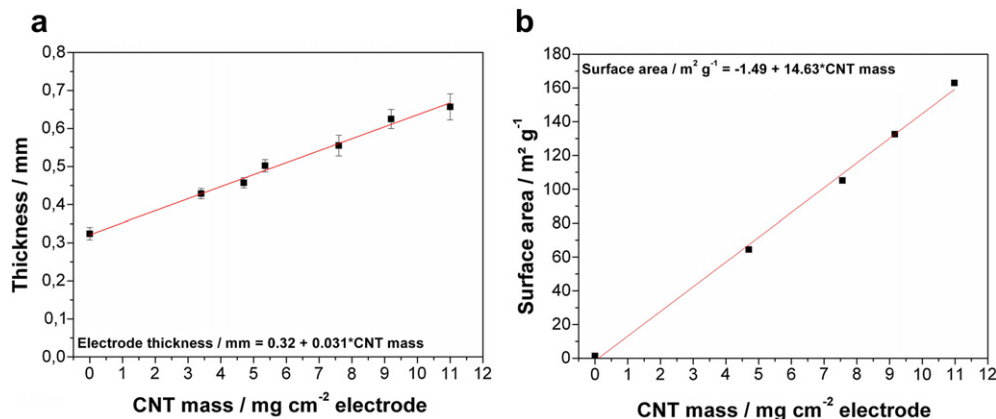
### 3.2. Electrode thickness

The electrode thickness is an important value to assemble a battery cell. Fig. 3a demonstrates the thickness increase of the original electrode in dependency of the CNT mass and a constant pressure of  $1.9 \text{ N cm}^{-2}$ . The electrode thickness seems to increase linearly with the CNT mass. The uncoated carbon substrate has a dimension of  $324 \mu\text{m}$ ; for every  $\text{mg CNT per cm}^2$  electrode the thickness of the electrode is increased by  $31 \mu\text{m}$ . Nevertheless, the electrode can be easily compressed to lower thickness values simply by increasing the pressure on it. By this means the total electrode dimension and therefore the electrode porosity in a cell can be easily adjusted.

### 3.3. Surface area vs. capacity

The conductive surface area is an extremely important value for a sulfur cathode. During charge and discharge the active material is

liquid in a broad voltage area and has to be transformed to solid sulfur at the end of charge or  $\text{Li}_2\text{S}$  at the end of discharge. For these final solid products a sufficient conductive electrode surface area has to be provided in order to avoid an interruption of the reaction before the highest obtainable capacity is reached. On contrary a surface area being higher as necessary would not result in any capacity benefits with respect to the capacity diagrams given in Fig. 4. As a consequence there must be a thickness maximum of the isolating sulfur or  $\text{Li}_2\text{S}$  layer determined by the electrode surface and the active mass weight. If the active mass is too high for the electrode surface, a lower sulfur utilization is expected because the sulfur or  $\text{Li}_2\text{S}$  build-up will be determined by the resistance of the already existing sulfur or  $\text{Li}_2\text{S}$  layer. An active mass below the critical active mass-electrode surface relation must not necessarily lead to capacities of  $1672 \text{ mAh g}^{-1}$  since other factors such as electrode structure, reaction kinetics ( $\rightarrow$  applied current) and self discharge (shuttle mechanism [1]) must also be taken into account.



**Fig. 3.** a) Thickness measurements of an electrode in dependence of the CNT coating weight b) surface area in dependence of the CNT coating weight.



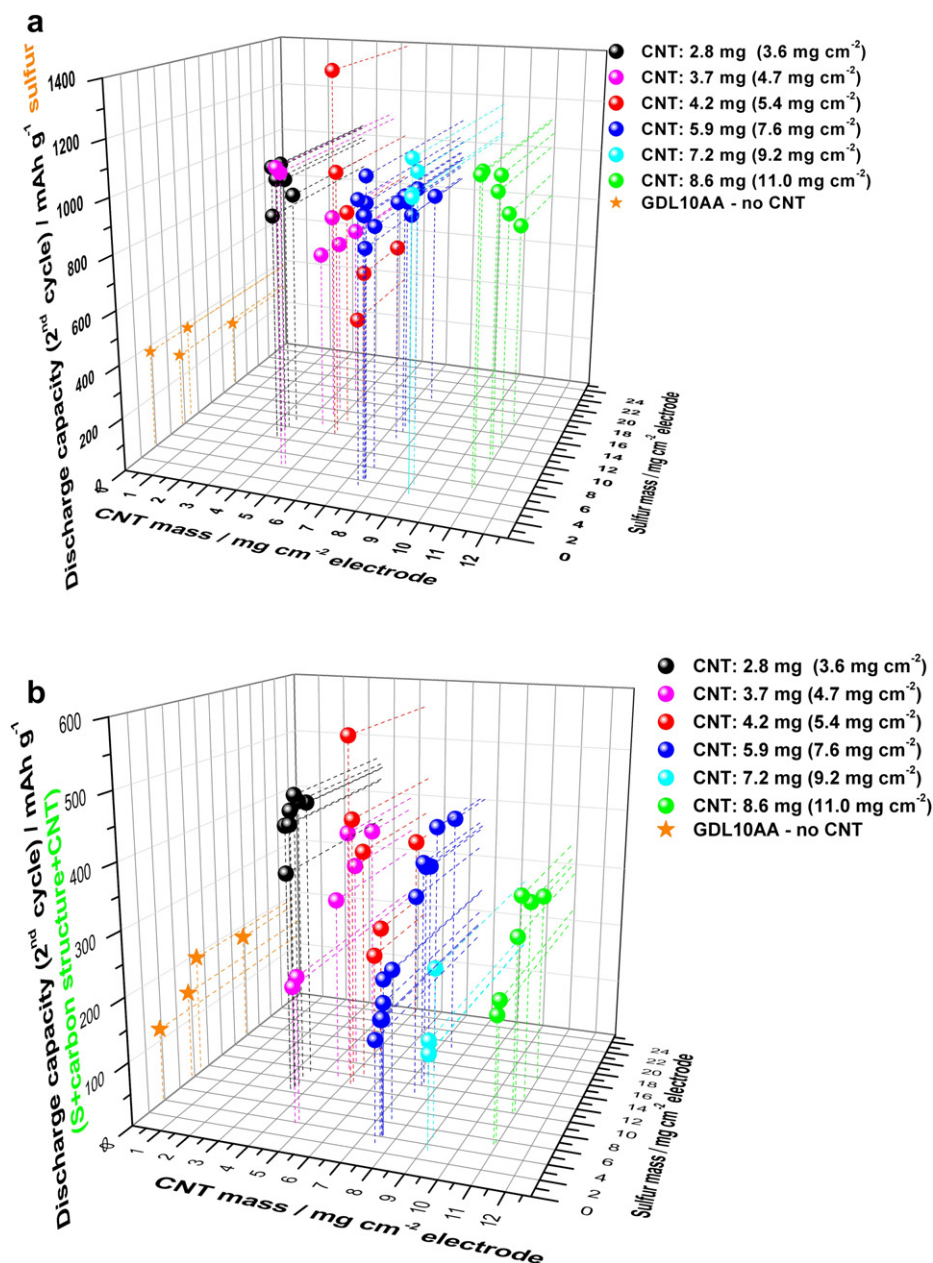
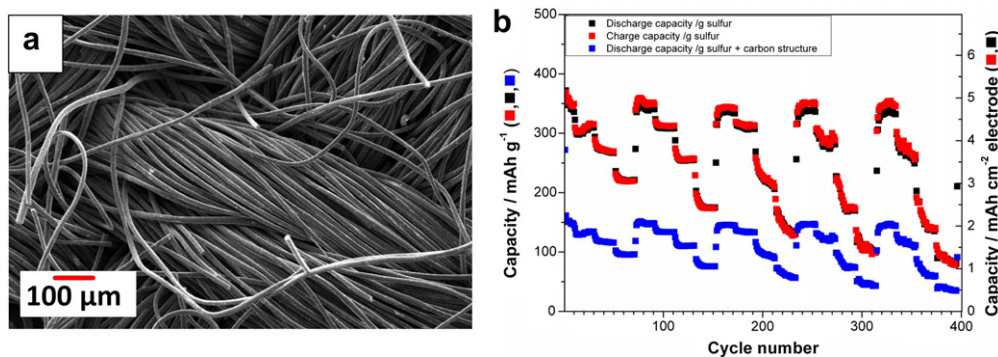


Fig. 4. Discharge capacity (2nd cycle) at  $0.64 \text{ mA cm}^{-2}$  electrode referred to the a) sulfur mass b) complete electrode mass (sulfur + CNT + carbon structure).

These factors are additionally influenced by the solubility of the polysulfides in the electrolyte making the choice of the electrolyte and its viscosity extremely important.

The surface area of an uncoated carbon structure was  $1.31 \text{ m}^2 \text{ g}^{-1}$ , which seems to be not enough to achieve the full possible capacity at an applied current of  $0.64 \text{ mA cm}^{-2}$  (compare Fig. 4a ★) since the capacities were only between 300 and  $400 \text{ mAh g}^{-1}$  sulfur. With every mg CNT coated on  $1 \text{ cm}^2$  electrode the surface is increased by  $14.63 \text{ m}^2$  (Fig. 3b). The sulfur utilization could be significantly increased from 300 to  $400 \text{ mAh g}^{-1}$  sulfur with no CNT on the electrode to values between 800 and  $1100 \text{ mAh g}^{-1}$  sulfur with CNT coating at various sulfur loads between 2 and  $20 \text{ mg cm}^{-2}$  (Fig. 4a). Even with very high sulfur loads the capacity referred to the sulfur mass stays above  $800 \text{ mAh g}^{-1}$ . Furthermore it could be proved, that surfaces of around  $50 \text{ m}^2 \text{ g}^{-1}$  electrode (CNT:  $3.6 \text{ mg cm}^{-2}$ ) are

enough to achieve capacities of around  $1000 \text{ mAh g}^{-1}$  at sulfur loads between 6 and  $9 \text{ mg cm}^{-2}$  electrode. Surface areas above this value did not increase the sulfur utilization, even if the sulfur mass was low ( $2\text{--}4 \text{ mg cm}^{-2}$ ). This verifies that additional factors like those discussed above seem to limit the sulfur utilization in a Li–S cell. To further investigate this hypothesis we melt infiltrated  $9.9 \text{ mg}$  sulfur per  $\text{cm}^2$  electrode in a Kynol 5092-20 carbon fibre cloth with a surface area of around  $1900 \text{ m}^2 \text{ g}^{-1}$ . From the SEM image (Fig. 5a) it seems that the structure is more closely packed in comparison to the GDL10AA (Fig. 2a). The resulting capacities with around  $350 \text{ mAh g}^{-1}$  at  $0.64 \text{ mA cm}^{-2}$  were clearly below the values achieved with all CNT coated carbon structures (Fig. 5b). This might be attributed to an easier access of the electrolyte dissolved polysulfides into the volume of the CNT coated electrode in comparison to the Kynol electrode.



**Fig. 5.** a) SEM image of a Kynol 5092-20 electrode in bird's eye view and b) capacity of a sulfur infiltrated Kynol 5092-20 vs. Li at various current loops ( $0.64 \text{ mA cm}^{-2}$ ,  $1.28 \text{ mA cm}^{-2}$ ,  $2.56 \text{ mA cm}^{-2}$ ,  $3.84 \text{ mA cm}^{-2}$ ). The sulfur mass was  $9.9 \text{ mg cm}^{-2}$  electrode.

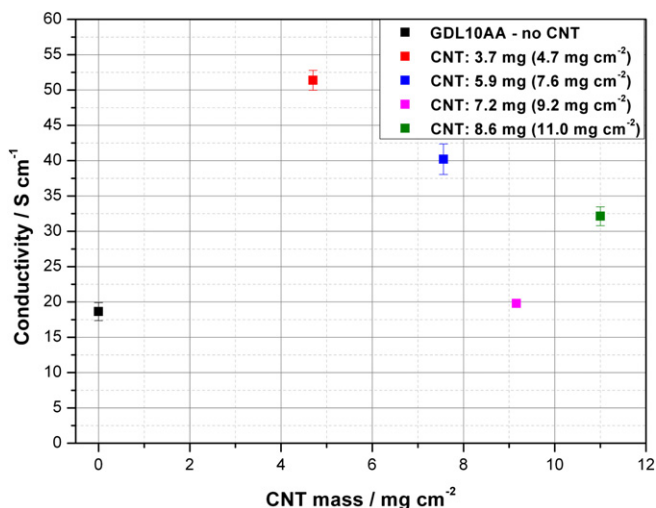
### 3.4. Electrode in plane conductivity and related capacity

Another reason for the lower capacity of the Kynol woven carbon electrode may be the electrode conductivity, which was around  $1 \text{ S cm}^{-1}$ . The CNT coated electrodes had higher conductivities of above  $18 \text{ S cm}^{-1}$  (Fig. 6). The CNT coating additionally increases the carbon structure conductivity. It seems to be that a low CNT mass is more beneficial than a high one since the measured conductivities were  $52 \text{ S cm}^{-1}$  for a CNT mass of  $4.7 \text{ mg cm}^{-2}$  and  $32 \text{ S cm}^{-1}$  for a CNT mass of  $11.0 \text{ mg cm}^{-2}$ . A CNT mass of  $9.2 \text{ mg cm}^{-2}$  leads to values of approximately  $20 \text{ S cm}^{-1}$  being higher than the bare carbon structure but lower than the expected value of around  $35 \text{ S cm}^{-1}$ . We believe that a low amount of CNT greatly increases the carbon structures conductivity by connecting the carbon fibre backbone in areas in which the carbon fibres are close to each other. A high CNT mass leads to a higher electrode thickness (compare Fig. 2, first row) – the CNT move the carbon fibres away from each other – but there are still some connections of carbon fibres through CNT leading to a higher overall conductivity than without CNT coating. Nevertheless, the measured in plane conductivity of the electrode should nearly have no effect on the material tests as can be seen in Fig. 7. The capacity diagrams over the cycle life show a high CNT mass (estimated lower conductivity) and a low CNT mass (estimated high conductivity) at various currents and sulfur loads. For comparable sulfur masses between 8 and  $9 \text{ mg cm}^{-2}$  (Fig. 7a,b), the achieved discharge capacity has the same level between 800 and  $900 \text{ mAh g}^{-1}$  sulfur

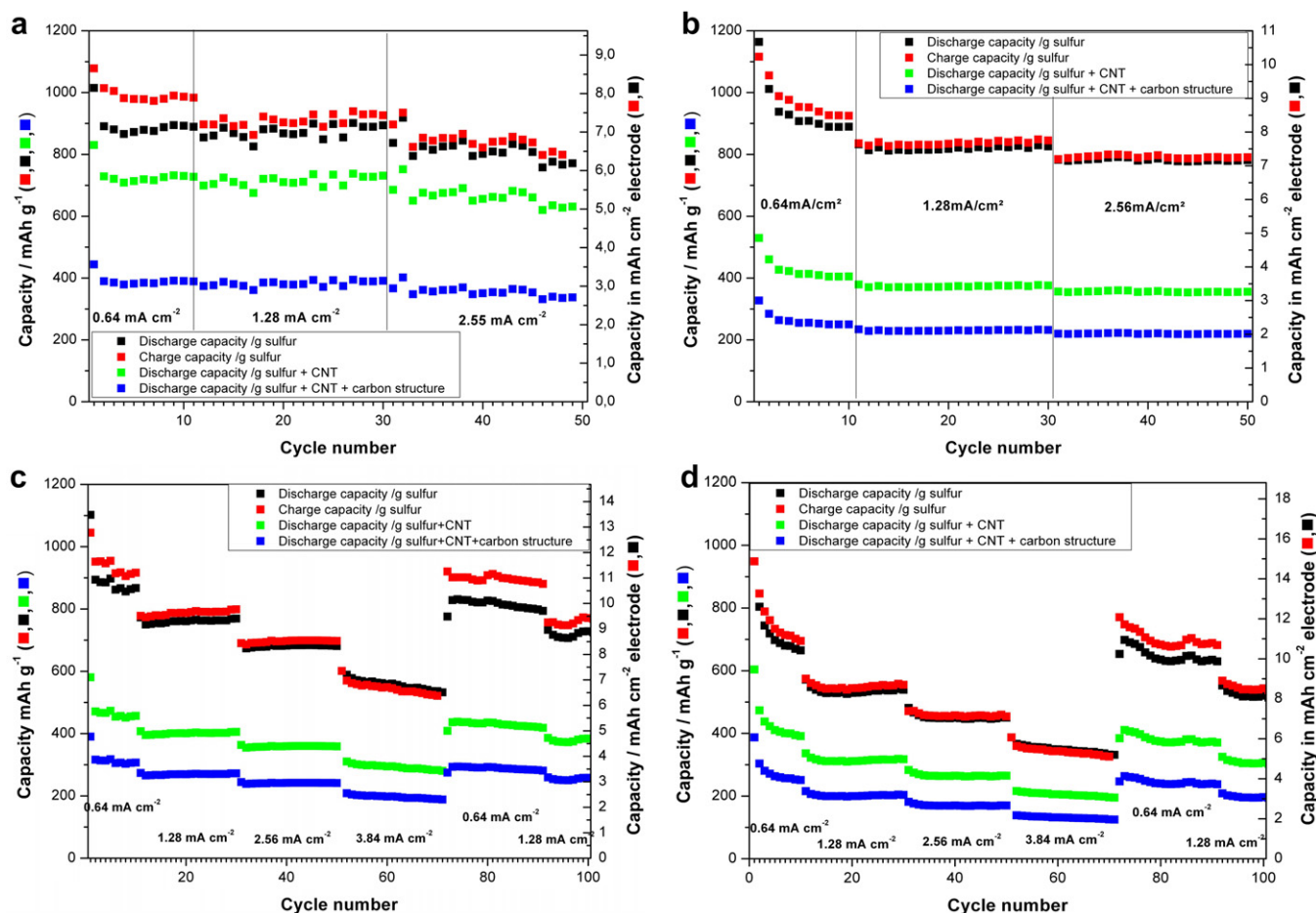
for all applied currents between  $0.64$  and  $2.56 \text{ mA cm}^{-2}$ . Additionally it is indicated that the capacity stays nearly constant even after increasing the current. The behaviour changes when the sulfur mass is increased to  $12.2$  or  $15.6 \text{ mg cm}^{-2}$  (Fig. 7c,d). Even though the sulfur utilization at  $12 \text{ mg cm}^{-2}$  is comparable to Fig. 7a and b at the lowest applied current of  $0.64 \text{ mA cm}^{-2}$ , the capacity drops clearly when the current is increased. With a sulfur mass of  $15.6 \text{ mg cm}^{-2}$  the achieved capacity related to the sulfur mass at  $0.64 \text{ mA cm}^{-2}$  is around  $700 \text{ mAh g}^{-1}$  compared to average  $900 \text{ mAh g}^{-1}$  at lower sulfur masses. At a higher current of  $2.56 \text{ mA cm}^{-2}$  the capacity is below  $500 \text{ mAh g}^{-1}$  compared to  $800 \text{ mAh g}^{-1}$  with lower sulfur masses. As a conclusion the in plane electrode conductivity had nearly no effect in our material test cells in which the electrodes were fully contacted by a stainless steel disk from below. Nevertheless we believe that the CNT-S electrodes can also be used without metal current collector in small commercial cells making the in plane conductivity extremely important. This would allow high energy densities since the achieved capacities referred to the sulfur mass, the CNT mass and the carbon structure mass can exceed the  $400 \text{ mAh g}^{-1}$  level (Figs. 4b and 7). For larger cells the CNT coated carbon structure electrode could be in support contacted by a very thin and coarse meshed aluminium current collector that has a lower weight than state of the art aluminium foil collectors. The sulfur mass on the electrode should be determined by the application conditions: With high sulfur masses (above  $12 \text{ mg cm}^{-2}$ ) the applied currents should not be too high, but with lower sulfur masses even “high rate” cells are imaginable.

### 3.5. Capacity in relation to the complete electrode with carbon current collector

In most publications so far the capacity was always referred to the sulfur mass. Regarding again that the sulfur fraction in the electrode is greatly diverse from publication to publication and regularly below the lithium-ion intercalation cathode level of 80%, it would be better to relate the capacity to the complete electrode and maybe additionally to the current collector. Figs. 4b and 7 demonstrate the capacity related to the sulfur mass, the CNT mass and the carbon “backbone” structure. As stated above an additional metal current collector is not absolutely necessary as long the applied current or the cell shape is not too large. It can be shown that the CNT coating definitely boosts the capacity from values between 100 and  $200 \text{ mAh g}^{-1}$  without CNT (Fig. 4b ★) to values that can be higher than  $400 \text{ mAh g}^{-1}$ . Additionally high electrochemically inactive CNT masses make only sense if the sulfur mass is also high. This can be best seen with a CNT mass of  $7.6 \text{ mg cm}^{-2}$  (●) in Fig. 4b. The capacity related to the complete electrode continuously increases with higher sulfur loads. Furthermore it



**Fig. 6.** Electrode in plane conductivity in  $\text{S cm}^{-1}$  in dependence of the CNT coating weight.



**Fig. 7.** Capacity over cycle life at various currents ( $0.64 \text{ mA cm}^{-2}$ ,  $1.28 \text{ mA cm}^{-2}$ ,  $2.56 \text{ mA cm}^{-2}$ ,  $3.84 \text{ mA cm}^{-2}$ ) in dependence of the CNT coating and sulfur active material weight a) S:  $8.0 \text{ mg cm}^{-2}$  and CNT:  $3.6 \text{ mg cm}^{-2}$ , b) S:  $9.2 \text{ mg cm}^{-2}$  and CNT:  $11.0 \text{ mg cm}^{-2}$ , c) S:  $12.2 \text{ mg cm}^{-2}$  and CNT:  $11.0 \text{ mg cm}^{-2}$ , d) S:  $15.7 \text{ mg cm}^{-2}$  and CNT:  $11.0 \text{ mg cm}^{-2}$ .

seems to be generally easier to achieve high capacities with lower CNT masses which can be obviously seen by comparing CNT masses of  $3.6 \text{ mg cm}^{-2}$  (●) with  $11.0 \text{ mg cm}^{-2}$  (●). Last but not least a low weight and perfectly tailored carbon backbone structure would also be beneficial to further increase the electrode-related capacity. We believe that an optimized system with optimal CNT mass, sulfur mass and ideal carbon backbone structure could have capacities higher than  $500 \text{ mAh g}^{-1}$  electrode with carbon current collector and currents of  $0.64 \text{ mA cm}^{-2}$ .

### 3.6. Voltage profile at various currents

Fig. 8 shows the voltage profile of a Li–S cell with  $9.2 \text{ mg cm}^{-2}$  sulfur and  $11.0 \text{ mg cm}^{-2}$  CNT at various currents ( $0.64 \text{ mA cm}^{-2}$ ,  $1.28 \text{ mA cm}^{-2}$ ,  $2.56 \text{ mA cm}^{-2}$ ,  $3.84 \text{ mA cm}^{-2}$ ) and cycle number. The capacity over cycle number of the corresponding cell is demonstrated in Fig. 7b. With increasing current a drop of the average discharge voltage and a rise of the average charge voltage can be observed. The voltage profile is characteristic for a DME:DIOX electrolyte with two plateaus. During the high level discharge plateau long chain polysulfides become reduced or decompose to medium chain polysulfides (e.g.  $\text{Li}_2\text{S}_4$ ). The latter are further reduced to soluble short chain polysulfides and insoluble polysulfides like  $\text{Li}_2\text{S}_2$  and  $\text{Li}_2\text{S}$  during the low level plateau. During charge those insoluble and soluble polysulfides are oxidized to medium chain polysulfides in the lower plateau which get afterwards oxidized to long chain polysulfides and  $\text{S}_8$  in the high plateau.

Regarding the green curve with the high current ( $3.84 \text{ mA cm}^{-2}$ ) it can be proved that lithium sulfur cells with binder free CNT sulfur cathode can be charged and discharged in below 2 h with good electrochemical results. The achieved capacity with  $\sim 750 \text{ mAh g}^{-1}$  sulfur and electrode surface capacity with around  $6.9 \text{ mAh cm}^{-2}$  electrode provide enough power for an EV combined with an acceptable charge time and interesting capacity.

### 3.7. Cycle stability and drawbacks

The obtained capacities can be stable over many cycles. We believe that the stability is on the one hand attributed to that there is no binder in the electrode which could degenerate due to the high volume change between  $\text{S}_8$  and  $\text{Li}_2\text{S}$ . On the other hand we suppose that the sulfur that takes not part in the reaction, step by step replaces the sulfur that was consumed by coating the lithium metal anode with insoluble  $\text{Li}_2\text{S}_y$  ( $y = 1, 2$ ) and  $\text{Li}_2\text{S}_y$  ( $y = 1, 2$ ) + electrolyte decomposition products. Cells that had higher sulfur utilizations above 75% (e.g. because of a lower current or a different type of electrode or separator, not shown here) faced capacity degradation every cycle, likely because there was no or less sulfur reserve left to compensate the loss of sulfur precipitating on the lithium metal anode.

The very high sulfur loads lead on the one hand to very high surface capacities of up to  $20 \text{ mAh cm}^{-2}$  electrode, but on the other hand to a severe short circuit risk through lithium dendrites. In most of our measurements these lithium dendrites limited the cycling to less than 100 cycles through a short circuit during



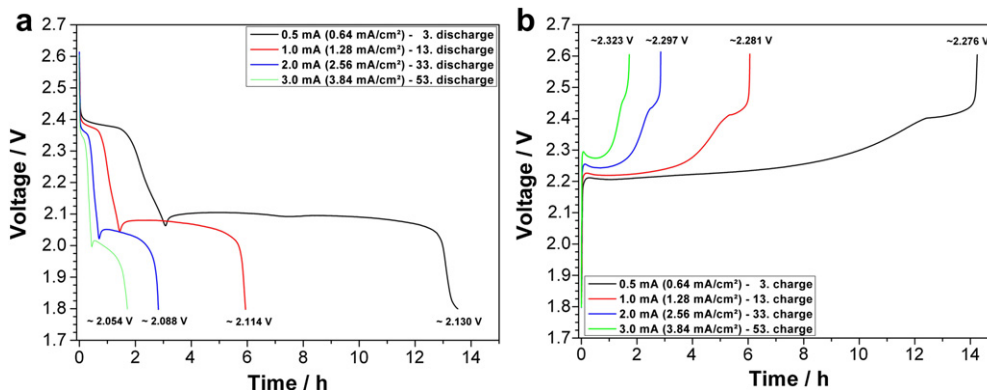


Fig. 8. Discharge a) and charge b) of a Li-S cell with  $9.2 \text{ mg cm}^{-2}$  sulfur and  $11.0 \text{ mg cm}^{-2}$  CNT at various currents.

charging. Obviously a specially designed separator is required for these high capacity electrodes. As an alternative an impermeable solid state ceramic could be used as already discussed in Ref. [7]. Since the conductivities of those ceramics are clearly below the values of liquid electrolytes combined with a much higher thickness compared to polyolefine separators, the applicable currents are low. Examinations of lithium metal anode dendrite formation and lithium sponge creation will be published elsewhere.

### 3.8. 18650 Cell pricing

Many carbon nanomaterials e.g. mesoporous carbon produced through templates are expensive and frequently difficult to be provided in larger batches. CNTs are already used in battery electrodes and can increase the cycle life through a better electrical contact of the active material by compensating the volume change during charge and discharge. Nevertheless, the here described CNT electrodes were produced by a CVD process that has to compete with conventional sulfur slurry technique cathodes. In order to determine whether the CNT electrode concept could be realized in the future we estimated the 18650 cell prices for a state of the art NCA-Graphite lithium ion intercalation system, a sulfur slurry electrode vs. lithium metal, a CNT sulfur electrode with carbon current collector and various sulfur loadings vs. lithium and a CNT sulfur electrode with aluminium current collector vs. lithium. Most prices of the cell material were taken from Howard et al. [8]. The lithium metal anode price is estimated with  $100 \text{ \$ kg}^{-1}$ . The sulfur price should be in the range between  $0.6 \text{ \$ kg}^{-1}$  (U.S. Geological Survey, 2009) for unpurified sulfur and  $24 \text{ \$ kg}^{-1}$  for pure sulfur with lab scale cost (SIGMA Aldrich). For small series industrial production a sulfur price of  $4 \text{ \$ kg}^{-1}$  has been taken for the calculations. This price could be reduced to  $0.6 \text{ \$ kg}^{-1}$  for future sulfur cathode mass productions. The price of carbon structures is difficult to determine because various types (e.g. woven carbon fibres, gas diffusion layers, carbon felts) with highly diverse prices exist. To achieve comparable electrochemical results a well ordered structure may be beneficial. As a result a high price of  $50 \text{ \$ m}^{-2}$  was chosen for the carbon structure in the first calculations. In a second more optimistic calculation a price of  $25 \text{ \$ m}^{-2}$  was chosen which should be a realistic price for a mass production. The price of the CNT coating per  $\text{m}^2$  is estimated with  $4 \text{ \$}$  for the liquid precursor,  $8 \text{ \$}$  for the gas precursor and  $4 \text{ \$}$  for energy ( $=16 \text{ \$ m}^{-2}$ ).

Additional assumptions:

- Coating length (both current collector sides): 118 mm.
- Capacities:  $1000 \text{ mAh g}^{-1}$  sulfur,  $220 \text{ mAh g}^{-1}$  NCA,  $370 \text{ mAh g}^{-1}$  graphite.
- Slurry cathode and slurry anode composition:

- 80% NCA, 10% carbon, 10% polymer
- 70% sulfur, 20% carbon, 10% polymer
- 90% graphite, 10% polymer
- Lithium mass was calculated to be twice the calculated theoretical sulfur cathode capacity (100% excess).
- Average discharge cell voltage of NCA vs. graphite: 3.65 V; lithium vs sulfur: 2.15 V.
- Fixed achieved capacity of  $6 \text{ mAh cm}^{-2}$  (double side coated), higher with sulfur masses above  $6 \text{ mg cm}^{-2}$ .
- Al current collector ( $14 \text{ }\mu\text{m}$ ), Cu current collector ( $10 \text{ }\mu\text{m}$ ) or carbon structure with  $8 \text{ mg cm}^{-2}$ .
- Electrolyte volume was determined by the free pore volume of the electrodes (30% for graphite anode, 30% for NCA cathode, 50% for conventional sulfur slurry cathode, 50% for CNT coated carbon structure sulfur cathode, 30% for lithium metal anode) and the free pore volume of the separator (40% porosity,  $25 \text{ }\mu\text{m}$  thickness).

It should be noted that the calculated prices are highly dependent on the assumptions made above.

The calculations led to a specific 18650 cell capacity of around 2.2 Ah for the NCA-graphite cell and all sulfur cells with sulfur load of  $6 \text{ mg cm}^{-2}$ . Sulfur loads of  $10 \text{ mg cm}^{-2}$  led to 3.7 Ah and  $15 \text{ mg cm}^{-2}$  to 5.6 Ah respectively. The specific cell energy was 8.1 Wh for the NCA-graphite cell. Sulfur masses of  $6 \text{ mg cm}^{-2}$  electrode led to energies below this value (4.8 Wh) on 18650 cell level because of the lower cell voltage. With sulfur masses of  $15 \text{ mg cm}^{-2}$  the cell energy of about 12 Wh was above this value. The capacity, energy and average cell voltage are summarized in Table 1.

The costs per component for a 18650 cell are demonstrated in Table 2. By using elemental sulfur as cathode material the costs could be drastically reduced in comparison to intercalation electrodes (here NCA). As a result the material costs for a 18650 sulfur slurry cathode with 11 cents are lower than the costs of a 18650 NCA cathode with 42 cent. But it has to be stated that only low cost conductive carbon was considered for this calculation. If specially tailored carbon (e.g. CMK-3) is used for the sulfur cathode, the costs should be clearly above this value. Nevertheless Schneider et al. already demonstrated, that high cost carbon is not necessary to achieve good electrochemical results [9].

In contrast, the CNT coated carbon structure sulfur cathodes have several times higher costs with around 2.45 \$. Responsible for these high costs is merely completely the carbon structure (75%) and the CNT coating process (24%), since no binder or conductive carbon are necessary. By using a CNT coated aluminium current collector instead of an expensive carbon structure the total CNT-sulfur cathode cost can be reduced to 60 cent. However, the CNT

**Table 1**

Capacity, energy and average cell voltage of a 18650 cell with NCA-graphite system and various lithium–sulfur systems.

	NCA-cathode vs graphite anode 27.3 mg NCA cm <sup>-2</sup>	Sulfur slurry cathode vs. lithium 6 mg S cm <sup>-2</sup>	CNT-C sulfur cathode vs. 6 mg S cm <sup>-2</sup>	CNT-C sulfur cathode vs. lithium 10 mg S cm <sup>-2</sup>	CNT-C sulfur cathode vs. lithium 15 mg S cm <sup>-2</sup>	CNT-Al sulfur cathode vs. lithium 6 mg S cm <sup>-2</sup>
Cell capacity in Ah (theoretic value)	2.68	3.72	3.72	6.19	9.29	3.72
Cell capacity in Ah (specific value)	2.22	2.22	2.22	3.70	5.56	2.22
Average cell voltage in V	3.65	2.15	2.15	2.15	2.15	2.15
Cell energy in Wh (theoretic value)	9.77	7.99	7.99	13.32	19.98	7.99
Cell energy in Wh (specific value)	8.11	4.78	4.77	7.96	11.95	4.78

coating on aluminium is complex because of the low melting point of the aluminium that prevents high working temperatures. A low working temperature, slightly below the melting point leads to a longer coating process, since CNT growth is inhibited.

The separator costs are comparable for all cells because the coating length is the same. Expenses for the graphite and the lithium metal anode are in the range of 19 cent as long as the sulfur mass is 6 mg cm<sup>-2</sup>. Higher sulfur loads of 10 or 15 mg cm<sup>-2</sup> lead to higher lithium metal anode costs of 32 cent or 48 cent respectively. If the lithium excess can be waived in the future by solving problems like dead lithium or dendritic growth, the costs of the lithium metal anode could be halved.

Another big cost factor in the cell is the electrolyte. The amount of electrolyte needed for the 18650 cell was calculated by using the electrode pore volume and an average electrolyte density of 1.2 g cm<sup>-3</sup>. A higher amount of electrolyte for the CNT coated carbon structure electrodes is estimated and calculated in comparison to the slurry cathodes but may not be needed necessarily, since the CNT carbon electrode's porosity can be adjusted by external pressure. The electrolyte amount for the carbon structure electrodes could be therefore reduced under circumstances. The lithium metal anode porosity was estimated with 30% although it should be around 0% in the beginning before the first discharge, when there are no dendrites, no lithium sponge and just the plane metal surface. Nevertheless, after some dozen cycles we estimate a higher, dendritic lithium surface which leads to lithium and electrolyte consumption through SEI creation and pores that need

to be filled with electrolyte. The weight ratio of electrolyte/sulfur in the sulfur cells was between 1.8 and 3.0 which can be considered as a low amount of electrolyte.

The costs of a copper current collector with a thickness of 10 µm will be around 9 cent for every 18650 cell. Maybe these costs need to be increased by some cents for the lithium sulfur cells because it is likely that copper mesh will be used together with lithium metal anodes and copper mesh should be typically more expensive than copper foil. Copper mesh provides the advantage of a good mechanical connection to the lithium metal anode. Nevertheless, it is also possible to use copper foil as current collector. The costs of the aluminium current collector will be around 3 cents and were saved for the CNT-carbon structure electrodes which should not be in need for an additional metallic current collector at lower currents. The cell housing was priced with 8 cent. It should be kept in mind that all prices for metal and further battery components may fluctuate and can be some cents higher or lower in the future.

Through accumulation of all costs the total material price for a 18650 cell was received. The process costs were estimated with around 30% of the total cell costs. Generally the process costs to produce a 18650 cell are dependent on the used technology, overhead and working cost and are considered to be between 20 and 40% of the total cell cost [10,11]. All in all the process costs for the NCA-graphite cell are estimated to be 50 cent. The process costs of a lithium-sulfur cell was estimated to be the same. The process costs for the CNT carbon structure electrode was estimated to be a little cheaper with 40 cents, since high process costs were already

**Table 2**Cost per component, cost per 18650 cell and cost per kWh<sup>-1</sup> of NCA-graphite and various lithium–sulfur systems.

Cost per Component in \$	NCA-cathode vs graphite anode 27.3 mg NCA cm <sup>-2</sup>	Sulfur slurry cathode vs. lithium anode 6 mg S cm <sup>-2</sup>	CNT-C sulfur cathode vs. lithium 6 mg S cm <sup>-2</sup>	CNT-C sulfur cathode vs. lithium 10 mg S cm <sup>-2</sup>	CNT-C sulfur cathode vs. lithium 15 mg S cm <sup>-2</sup>	CNT-Al sulfur cathode vs. lithium 6 mg S cm <sup>-2</sup>
Active material (cathode)	0.353	0.009	0.009	0.015	0.022	0.009
Binder	0.058	0.102	0.000	0.000	0.000	0.000
Conductive carbon	0.006	0.003	0.000	0.000	0.000	0.000
Carbon structure	0.000	0.000	1.852	1.852	1.852	0.000
CNT coating process	0.000	0.000	0.593	0.593	0.593	0.593
Total cost cathode	0.418	0.114	2.454	2.460	2.467	0.602
Separator	0.091	0.091	0.089	0.089	0.089	0.089
Graphite anode	0.189	0.000	0.000	0.000	0.000	0.000
Lithium anode (100 % excess)	0.000	0.192	0.192	0.321	0.481	0.192
Electrolyte	0.267	0.260	0.411	0.485	0.579	0.251
Cu current collector (10µm)	0.085	0.085	0.085	0.085	0.085	0.085
Al current collector (14µm)	0.028	0.028	0.000	0.000	0.000	0.087
Housing	0.080	0.080	0.080	0.080	0.080	0.080
Material cost	1.16	0.85	3.31	3.52	3.78	1.39
Process cost (~30 %)	0.50	0.50	0.40	0.40	0.40	0.40
Total cost (18650 cell)	1.65	1.35	3.71	3.92	4.18	1.78
Cost in \$ kWh <sup>-1</sup>	203.90	281.78	775.63	491.61	349.60	372.75
Cost in \$ kWh <sup>-1</sup> (1200 mAh g <sup>-1</sup> sulfur)	-	234.81	646.36	409.68	291.34	310.63
Cost in \$ kWh <sup>-1</sup> (1000 mAh g <sup>-1</sup> sulfur; 25 \$ m <sup>-1</sup> carbon structure price)	-	-	581.83	375.34	272.08	372.75
Cost in \$ kWh <sup>-1</sup> (1200 mAh g <sup>-1</sup> sulfur; 25 \$ m <sup>-1</sup> carbon structure price)	-	-	484.86	312.78	226.74	310.63



taken into account in the CNT coating process which already leads to an operational sulfur cathode.

To summarize the calculations it can be stated that lithium–sulfur cells with sulfur slurry cathode will be the cheapest 18650 cell with 1.35 \$ total manufacturing costs. The NCA-graphite cell will cost around 1.65 \$ being in good agreement with the calculations in Ref. [10] with prices of around 1.70 \$ for a LiCoO<sub>2</sub> system. The CNT coated carbon structure sulfur cathode cells nearly have three times the price of a conventional sulfur slurry cathode cell. This is mainly attributed to the very high estimated costs of the carbon structure with 50 \$ m<sup>-2</sup>. By using an aluminium current collector the total cell costs of 1.78 \$ are merely comparable to the NCA-graphite system. Regarding the costs per kWh the ranking changes. Now the NCA-graphite system has the lowest effort with 204 \$ kWh<sup>-1</sup> followed by the sulfur slurry cathode system with 282 \$ kWh<sup>-1</sup>. The prices of the CNT coated carbon structure cells are considerably higher but the cost reducing effect of higher sulfur loads per cm<sup>2</sup> electrode are clearly visible. By adding 15 mg sulfur per cm<sup>2</sup> electrode, which is a practicable load (compare Figs. 4 and 7) for a CNT coated carbon structure electrode the cell costs are now only 25% higher in comparison to the conventional lithium–sulfur cell. Generally the costs per kWh for the lithium–sulfur cells are higher than in the NCA-graphite cell. This is due to the higher cell voltage of the latter, leading to higher comparable cell energies (Table 1), reducing the costs per kWh.

In order to examine the influence of higher sulfur utilizations in future lithium–sulfur cells we changed our calculation assumption by increasing the achievable capacity from 1000 to 1200 mAh g<sup>-1</sup> sulfur. By doing so the costs per kWh greatly drop between 50 and 130 \$ kWh<sup>-1</sup> depending on sulfur load and cathode type (Table 2). The energy cost of the sulfur slurry cathode cell and the carbon structure sulfur cathode with 15 mg sulfur per cm<sup>2</sup> are now only 31 \$ kWh<sup>-1</sup> or 87 \$ kWh<sup>-1</sup> higher than the energy costs of the NCA-graphite cell. Regarding the high estimated prices of the carbon structure (50 \$ m<sup>2</sup>) a more optimistic scenario was added to the calculation in which the carbon structure only costs 25 \$ m<sup>2</sup>. The costs per kWh can now be reduced greatly for the CNT coated carbon structures and can even fall below the costs of conventional sulfur slurry cathode cells (227 \$ kWh<sup>-1</sup> for 15 mg sulfur per cm<sup>2</sup> electrode and 1200 mAh g<sup>-1</sup> sulfur).

As a conclusion lithium–sulfur cells will be cheaper than state of the art lithium-ion intercalation cells. Nevertheless, the costs per energy can be higher unless the cell capacity of the lithium–sulfur cells can exceed the intercalation cell capacity. This could be done through higher sulfur loads above 3 mg sulfur per cm<sup>2</sup> electrode and/or higher coating lengths through thinner lithium metal anodes compared to graphite anodes. A way to greatly increase the sulfur load are the here introduced CNT coated carbon structure electrodes. If a cheap carbon structure suitable for sulfur cathodes (low weight, homogeneous structure, good electrochemical results) can be identified, the energy costs for such a 18650 cell may be lower than with a sulfur slurry cathode with “only” 3 mg sulfur per cm<sup>2</sup> electrode. Additionally it must be kept in mind that the here calculated prices for the lithium–sulfur cells can be greatly reduced by removing the assumed 100% excess of lithium. An optimized and

perfectly designed future lithium–sulfur cell is likely to have comparable or lower costs per kWh than a lithium-ion intercalation cell. Additionally the lithium–sulfur cell may have two or three times the energy density.

#### 4. Conclusion

A binder free CNT coated carbon structure electrode was introduced. The sulfur loads can be several times higher than in all so far published sulfur cathodes. The electrochemical results can be stable for 100 cycles and more if shortcuts by lithium dendrites can be avoided. The achieved capacities depend on the sulfur load and the applied current and are between 800 and 900 mAh g<sup>-1</sup> sulfur at 0.64 mA cm<sup>-2</sup>. The capacities related to the sulfur mass, the CNT mass and the carbon structure mass can be higher than 400 mAh g<sup>-1</sup>. High electrode surfaces above 100 m<sup>2</sup> g<sup>-1</sup> seem to be unnecessary to enable high sulfur loads with good sulfur utilization. The structure of the electrode seems to have a higher effect and should be receivable for the electrolyte and polysulfides. The in plane conductivity of the CNT coated carbon structure cathode plays a minor role in our test cells but should play a major role if the metallic current collector should be spared in order to increase the energy density. The price of 18650 cells with CNT coated carbon sulfur electrodes vs. lithium can become market ready if the price for the carbon structure itself can be reduced (10–25 \$ m<sup>-2</sup>) and can compete with state of the art lithium-ion cells or conventional sulfur slurry cells as long as the sulfur load is high.

#### Acknowledgements

This research was financed by the German Bundesministerium für Bildung und Forschung (BMBF) through the project STROM: “AlkaSuSi-Alkalimetall sulfur and silicon”. We are grateful for the support. We would further like to thank Jan Tomforde (BASF) and Holger Schneider (BASF) for discussing the integrity of the price calculation.

#### References

- [1] Y.V. Mikhaylik, J.R. Akridge, *Journal of the Electrochemical Society* 151 (11) (2004) A1969–A1976.
- [2] M. Rao, W. Li, E.J. Cairns, *Electrochemistry Communications* 17 (2012) 1–5.
- [3] J. Schuster, G. He, B. Mandlmeier, T. Yim, K.T. Lee, T. Bein, L.F. Nazar, *Angewandte Chemie International Edition* 51 (2012) 3591–3595.
- [4] S.S. Zhang, J.A. Read, *Journal of Power Sources* 200 (2012) 77–82.
- [5] S. Dörfler, A. Meier, S. Thieme, P. Németh, H. Althues, S. Kaskel, *Chemical Physics Letters* 511 (2011) 288–293.
- [6] S. Dörfler, M. Hagen, H. Althues, J. Tübke, S. Kaskel, M.J. Hoffmann, *Chemical Communications* 48 (2012) 4097–4099.
- [7] M. Hagen, S. Dörfler, H. Althues, J. Tübke, M.J. Hoffmann, S. Kaskel, K. Pinkwart, *Journal of Power Sources* 213 (2012) 239–248.
- [8] W.F. Howard, R.M. Spotnitz, *Journal of Power Sources* 165 (2007) 887–891.
- [9] H. Schneider, A. Garsuch, A. Panchenko, O. Gronwald, N. Janssen, P. Novák, *Journal of Power Sources* 205 (2012) 420–425.
- [10] L. Gaines, R. Cuenca, *Costs of Lithium-ion Batteries for Vehicles*, Argonne National Laboratory, Center for Transportation Research, 2000.
- [11] M. Anderman, *Market and Batteries for Electrified Vehicles: Can We De-emphasize the Battery Cost Discussion for Now?* (2012) (Advanced Automotive Batteries).